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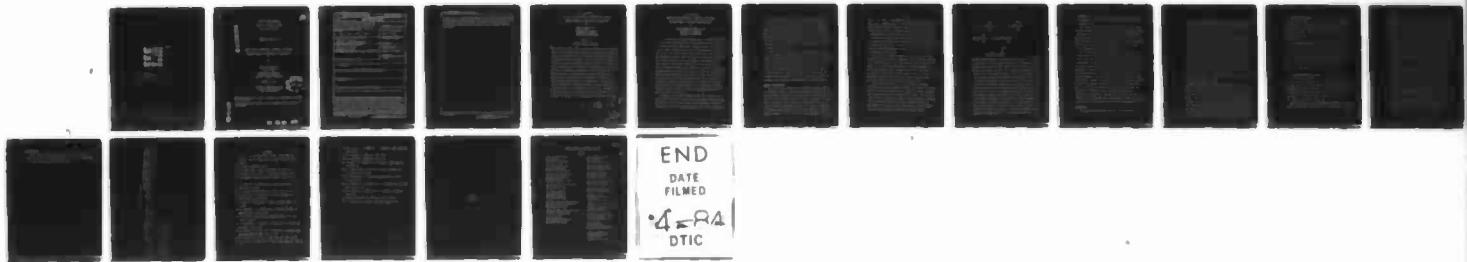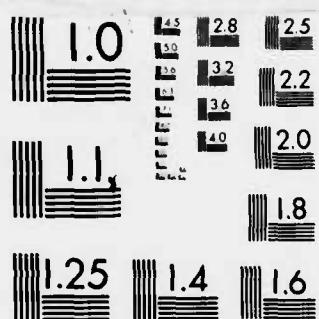
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AEROSOL DIRECT FLUORINATION: SYNTHESES OF THE HIGHLY

BRANCHED KETONES, F-PINACOLONE and "F-PROVALONE"

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The extension of aerosol direct fluorination techniques to the syntheses of the here-to fore unknown highly branched perfluoroketones F-3,3-dimethyl-2-butanone (F-pinacolone) and F-2,2,5-trimethyl-3-hexanone ("F-provalone") from 3,3-dimethyl-2-butanone (pinacolone) and 2,2,4,4-tetramethyl-3-pentanone (pivalone)respectively demonstrates again the efficacy of the aerosol direct fluorination process for the synthesis of perfluoroketones directly from ketones. The interesting rearrangement of the hydrocarbon di-tert-butyl ketone (pivalone) to the perfluorinated tert-butyl iso-butyl ketone, "F-provalone" is unprecedented in our experience

and does not occur at the monofluorination step but later in the fluorination. Isolated yields of 12% and 9% though modest are unadjusted by physical losses of recoverable hydrocarbons present at the termination of the reaction. Perfluorinated product distributions, concentrations of products collected from the reactor effluent, are 23% and 71% of the total material traversing the reactor.

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BRANCHED KETONES, F-PINACOLONE AND "F-PROVALONE"

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The extension of aerosol direct fluorination techniques to the syntheses of the here-to-fore unknown highly branched perfluoroketones F-3,3-dimethyl-2-butanone (F-pinacolone) and F-2,2,5-trimethyl-3-hexanone ("F-provalone") from 3,3-dimethyl-2-butanone (pinacolone) and 2,2,4,4-tetramethyl-3-pentanone (pivalone) respectively demonstrates again the efficacy of the aerosol direct fluorination process for the synthesis of perfluoroketones directly from ketones. The interesting rearrangement of the hydrocarbon di-tert-butyl ketone (pivalone) to the perfluorinated tert-butyl iso-butyl ketone, "F-provalone" is unprecedented in our experience and does not occur at the monofluorination step but later in the fluorination. Isolated yields of 12% and 9% though modest are unadjusted by physical losses of recoverable hydrocarbons present at the termination of the reaction. Perfluorinated product distributions, concentrations of products collected from the reactor effluent, are 23% and 71% of the total material traversing the reactor.

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Aerosol Direct Fluorination: Syntheses of the Highly

Branched Ketones, F-Pinacolone and F-Pivalone

by

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The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation. The application of this process to alkanes, ethers, cycloalkanes, and ketals has been demonstrated.[1] Extension of this noval process to ketones has provided direct access to analog perfluoroketones in modest yields, and has led to the successful perfluorination of methyl ketones[2] as well as both symmetric and unsymmetric long chain ketones.[3] Aerosol direct fluorination of the cycloalkyl methyl ethers or cycloalkyl ethylene glycol ketals have produced the corresponding perfluorinated analogs, which can be converted in good yields to the corresponding perfluorocycloketones via treatment with 100% sulfuric acid.[4] We report here the aerosol direct fluorination of the highly branched ketones 3,3-dimethyl-2-butanone (pinacolone) and 2,2,4,4-tetramethyl-3-pentanone (pivalone); aerosol direct fluorination of 2,2,4,4-tetramethyl-3-pentanone results in the first example of a skeletal rearrangement occuring during the aerosol fluorination of ketones.

In general, routes to perfluoroketones, other than the aerosol direct fluorination process, require either the prior preparation of highly chlorinated species, or (in most cases) highly fluorinated species. The Swarts reaction and other reactions involving halogen exchange require preparation

of the corresponding chlorocarbons prior to fluorination, and the higher
perchlorocarbons are often difficult to prepare. Typical preparations of
perfluoro ketones include the decomposition over Lewis acid catalysts of
perfluoroalkyene epoxides[6-13] and the reaction of perfluoroalkyl carbox-
ylates or perfluoroacyl chlorides with organometallic reagents such as
perfluoropropyl lithium, perfluoropropyl magnesium iodide, or perfluoropropyl
zinc iodide.[14-18] In contrast to the above, the aerosol direct fluorina-
tion method has provided direct access to perfluoroketones from the relative-
ly inexpensive hydrocarbon analogs.[3]

Whereas a number of straight chain perfluoro ketones are known, rela-
tively few branched perfluoroketones are known. The fluoride ion catalyzed
addition of perfluoroacyl fluorides to F-propene affords a route to perfluoro
ketones containing the branched perfluoroisopropyl group,[19-23] and these
represent the majority of the known branched perfluoroketones. Only two
other branched perfluoroketones have been reported in the literature:
F-4-methyl-2-pentanone, formed via the Lewis acid catalyzed opening of
F-3-methyl-2-butenyl epoxide[10] and F-4-methyl-2-heptanone, formed via the
treatment of F-2-chlorosulfato-4-methylheptane with potassium fluoride.[24]

Results and Discussion

The aerosol direct fluorination of 3,3-dimethyl-2-butanone produced
F-3,3-dimethyl-2-butanone, 3-difluoromethyl-F-methyl-2-butanone and 3,3-bis-
(difluoromethyl)-F-2-butanone as the major products, constituting 23%, 25%,
and 12% of the total products collected by weight, respectively. The aerosol
system is dependent on the generation of a particulate aerosol that is
ideally crystalline, monodisperse, and with little tendency to aggregate. If
the conditions considered ideal are met, percent yields based on throughput
(amounts injected) and product (collected) percent distributions will differ

by only a few percent. As deviations from this ideality occur, the percent yields based on throughput begin to fall due to physical losses within the aerosol generator and initial reaction stage (see ref 1). These losses can be significant and result in sometimes significant amounts of unfluorinated or complex mixtures of generally less than trifluorinated products collected at the close of the reactions when the system warms to ambient or is opened for cleaning between reaction runs. Although significant advances in optimization have been made, this is as much art as science. If no corrections are made due to recovered unreacted or partially reacted materials, the yield of F-3,3-dimethyl-2-butanone was 12%.

The isolation of significant quantities of the mono- and di-hydryl products reflects the sterically crowded nature of the fluorinated tert-butyl group; wherein replacement of the final hydrogens becomes increasingly difficult due to increased fluorine shielding of the residual hydrogens of the fluorinated tert-butyl group. It should be noted that in the aerosol direct fluorination of straight chain ketones the major product in all cases is the perfluorinated product; mono- and di-hydryl products typically amount to no more than a few percent of the total products collected.[2,3]

Aerosol direct fluorination of 2,2,4,4-tetramethyl-3-pentanone (pivalone) produced F-2,2,5-trimethyl-3-hexanone ("F-provalone") as the major product. This result represents the first example of a skeletal rearrangement occuring during the aerosol fluorination of ketones. Since the first step in the direct fluorination process involves the abstraction of hydrogen, it was originally proposed that this novel rearrangement involved a rearrangement of the initially formed primary radical to the more stable tertiary radical, followed by fluorination in the usual fashion:

$$F_2 \longrightarrow 2F\cdot$$

$$F\cdot \ + \ (CH_3)_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \longrightarrow HF \ + \ (CH_3)_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{\cdot CH_2}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

$$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{\cdot CH_2}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \longrightarrow (CH_3)_3C-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\cdot}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

$$\downarrow (F_2)$$

$$(CF_3)_3C-\overset{\overset{O}{\|}}{C}-CF_2-CF(CF_3)_2$$
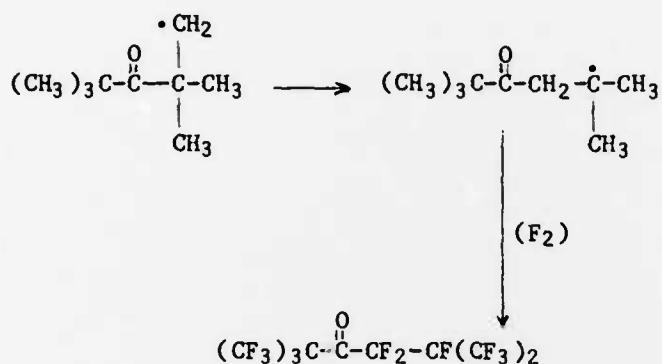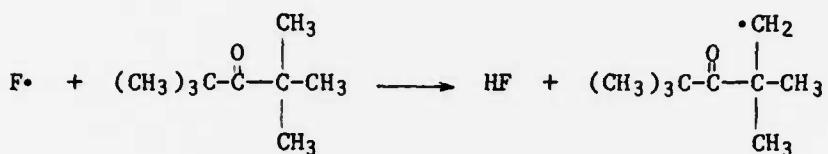
Subsequent experiments with a low concentration of fluorine (1:2 molar ratio of hydrocarbon to fluorine) showed however that the rearrangement must occur sometime after the first fluorine is added; the major product in these low fluorine runs (besides unreacted 2,2,4,4-tetramethyl-3-pentanone) is 1-fluoro-2,2,4,4-tetramethyl-3-pentanone, resulting from the simple replacement of hydrogen by fluorine and involving no rearrangement. The possibility of photolytic rearrangement of the starting material in the ultraviolet stage of the aerosol fluorination apparatus was also eliminated; reactions at low fluorine concentration both in the dark and with the operating ultraviolet stage produce 1-fluoro-2,2,4,4-tetramethyl-3-pentanone as the major product. The possibility of thermal rearrangement of the starting material in the flash evaporator/sublimator unit of the aerosol fluorination apparatus was also eliminated by subsequent experiments. For all the reactions at low fluorine concentrations only very small amounts of other fluorinated materials were present, but difficulty in separation and minimal quantities prevented their characterization. It would appear then that this

rearrangement occurs sometime after the introduction of the first fluorine. The elucidation of the mechanism of this noval rearrangement should prove to be interesting.

For a typical run at high fluorine concentrations, $\underline{F}$-2,2,5-trimethyl-3-hexanone constituted 71% of the total products collected by weight, without correcting for unreacted or partially reacted materials the percent yield based on the amount of 2,2,4,4-tetramethyl-3-pentanone injected was 9%. The majority of losses are due to physical losses within the reactor as evidenced by the finding of unreacted 2,2,4,4-tetramethyl-3-pentanone inside the reactor upon opening of the system for cleaning.

The ^{19}F nmr spectrum of $\underline{F}$-2,2,5-trimethyl-3-hexanone (see expt. section) consists of four multiplets of relative intensity 9:6:2:1 at $\emptyset$ = -61.61, -71.82, -109.32, and -184.26 ppm (1% $CFCl_3/CDCl_3$ internal standard), corresponding to the tert-butyl CF_3 groups, the remaining CF_3 groups, the CF_2 group, and the methine fluorine, respectively. The CF_2 group appears as a hexadectet of doublets at $\emptyset$ = -109.32 ppm due to coupling with all CF_3 groups and the methine fluorine. The hexadectet arises from the fact that the coupling constants of the CF_2 group with the two different type CF_3 groups are identical. Further confirmation of the structure is supplied by the mass spectrum. The chemical ionization mass spectrum includes intense peaks at m/e = 483, 467, and 447 corresponding to the molecular ion plus CH_5, the molecular ion plus hydrogen, and the molecular ion minus fluorine, respectively, in addition to a base peak at m/e = 219 due to the $C_4F_9^+$ fragment. The electron impact mass spectrum exhibits a peak at m/e = 447 due to the molecular ion minus fluorine and a consistent fragmentation pattern.

Experimental

The basic aerosol fluorinator design and a basic description of the

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.[1] A modified aerosol generator adapted to a flash evaporator fed by a syringe pump driving a 5 mL Precision Sampling Corp "Pressure Lok" Syringe was employed for the reactions.[25] Workup of products following removal of hydrogen fluoride consisted of vacuum line fractionation, infrared assay of fractions, gas chromatographic separation of components using either a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed Chromosorb P conditioned at 225°C (12 h) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb P, conditioned at 250°C (12 h). Following gas chromatographic separation (Bendix model 2300, subambient multicontroller) all products of significance were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry (PE 1330), electron impact (70 eV) and chemical ionization (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980A MS, 5934A computer) and ^1H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Aerosol Fluorination of 3,3-dimethyl-2-butanone. 3,3-Dimethyl-2-butanone (Aldrich) was used as received. A pump speed corresponding to 2.8 mmol/h was established and 0.8 mL 3,3-dimethyl-2-butanone was delivered over a 2.25 h period. Details of the aerosol fluorination parameters are given in Table 1. From the crude product was isolated 0.238 g (23%) F-3,3-dimethyl-2-butanone, 0.258 g (25%) 3-difluoromethyl-F-3-methyl-2-butanone, and 0.134 g (13%) 3,3-bis(difluoromethyl)-F-2-butanone (GLC temperature program on the QF-1 column; 0°C, 2 m; 1°C/m to 10°C; 10°C, 1 m; 20°C/m to 180°C). The yield of F-3,3-dimethyl-2-butanone based on 3,3-dimethyl-2-butanone injected was 12%. The characterization of these new compounds are given below.

F-3,3-Dimethyl-2-butanone. $CF_3{}^AC(O)C(CF_3{}^B)_3$: IR (cm^{-1}) 1770 (m), 1275 (vs), 1230 (s), 1200 (s), 1055 (w), 985 (m), 870 (m), 730 (m), 720 (m), 690 (w). Major mass cations were [m/e(int.)formula]: [CI] 317(59)$C_6F_{12}OH$, M+H; 297(84)$C_6F_{11}O$, M-F; 97(100)C_2F_3O; 69(58)CF_3: [EI] 181(16)C_4F_7; 97(21)C_2F_3O; 69(100)CF_3. ^{19}F NMR [1% $CFCl_3/CDCl_3$] ϕ_A = -73.88 ppm (d), ϕ_B = -61.12 ppm (q), J_{AB} = 6.1 Hz. Anal. Calcd for $C_6F_{12}O$: C, 22.80; F, 72.13. Found: C, 21.37; F, 72.43.

3-Difluoromethyl-F-3-methyl-2-butanone. $CF_3{}^AC(O)(CF_2{}^BH^C)(CF_3{}^D)_2$: IR (cm^{-1}) 3015 (w), 1760 (m), 1390 (m), 1370 (m), 1275 (vs), 1235 (vs), 1190 (s), 1135 (m), 1120 (m), 1065 (m), 1020 (w), 980 (s), 910 (w), 870 (s), 765 (m), 750 (m), 730 (s), 705 (m), 655 (m). Major mass cations were [m/e(int.)formula]: [CI] 300(8)$C_6F_{11}OH_3$, M+2H; 164(100)$C_4F_6H_2$; 97(15)C_2F_3O: [EI] 231(28)C_5F_9; 164(33)$C_4F_6H_2$; 160(61)C_4F_5OH; 97(50)C_2F_3O; 69(100)CF_3; 51(38)CF_2H. ^{19}F NMR [1% $CFCl_3/CDCl_3$] ϕ_A = -73.85 ppm (m), ϕ_B = -126.69 ppm (m), ϕ_D = -62.05 ppm (m). ^1H NMR δ_C = +6.63 ppm (t); J_{CF_2H} = 51.5 Hz.

3,3-Bis(difluoromethyl)-F-2-butanone. $CF_3{}^AC(O)(CF_3{}^B)(CF_2{}^CH^D)_2$: IR (cm^{-1}) 3010 (w), 1755 (m), 1365 (w), 1275 (w), 1250 (vs), 1225 (vs), 1190 (s), 1160 (m), 1130 (m), 1060 (m), 1020 (m), 900 (w), 870 (w), 730 (s). Major mass cations were [m/e(int.)formula]: [CI] 282(100)$C_6F_{10}OH_4$, M+2H; 212(36)$C_5F_7OH_3$; 97(65)C_2F_3O; 69(43)CF_3; [EI] 212(64)$C_5F_7OH_3$; 146(41)C_6F_3OH; 142(100)$C_4F_4OH_2$; 97(35)C_2F_3O; 69(85)CF_3; 51(43)CF_2H. ^{19}F NMR [1% $CFCl_3/CDCl_3$] ϕ_A = -74.61 ppm (m), ϕ_B = -62.99 ppm (m), ϕ_C = -125.18 ppm (m). ^1H NMR δ_D = +6.59 ppm (t); J_{CF_2H} = 52.7 Hz.

Aerosol Fluorination of 2,2,4,4-Tetramethyl-3-pentanone. 2,2,4,4-Tetra-methyl-3-pentanone (99%, Fluka Chemicals) was used as received. A pump speed

corresponding to 2.9 mmol/h was established and 1.0 mL 2,2,4,4-tetramethyl-3-pentanone delivered over a 2 hour period. Details of the aerosol fluorination parameters are given in Table 1. From the crude product (0.346 g) was isolated 0.246 g (71%) F-2,2,5-trimethyl-3-hexanone (GLC temperature program on the SE-52 gas chromatographic column: 30°C, 5 m; 5°C/m to 100°C; 100°C, 1 m; 20°C/m to 180°C). The yield of F-2,2,5-trimethyl-3-hexanone based on the amount of 2,2,4,4-tetramethyl-3-pentanone injected was 9%. Upon opening up the reactor for cleaning, significant amounts of unreacted 2,2,4,4-tetramethyl-3-pentanone were found. Runs with low fluorine concentrations (ultraviolet stage on or off) produced 1-fluoro-2,2,4,4-tetramethyl-3-pentanone as the major product. Characterizations of these compounds are given below.

F-2-2,5-Trimethyl-3-hexanone. $(CF_3{}^A)_3CC(O)CF_2{}^BCF^C(CF_3{}^D)_2$: IR (cm^{-1}) 1770 (m), 1270 (vs), 1205 (m), 1150 (m), 1140 (m), 1045 (m), 980 (s), 730 (s), 710 (m), 680 (m). Major mass cations were [m/e(int.)formula]: [CI] 483(2)$C_{10}F_{18}OH_5$, M+CH$_5$; 467(12)$C_9F_{18}OH$, M+H; 447(54)$C_9F_{17}O$, M-F; 247(55)C_5F_9O; 219(100)C_4F_9; 201(84)C_4F_8; 181(98)C_4F_7; 69(75)CF_3: [EI] 447(1)$C_9F_{17}O$, M-F; 247(37)C_5F_9O; 219(43)C_4F_9; 69(100)CF_3. ^{19}F NMR (1% CFCl$_3$/CDCl$_3$) ϕ_A = -61.61 ppm (t of m), ϕ_B = -109.32 ppm (hexadec of doublets), ϕ_C = -184.26 ppm (m), ϕ_D = -71.82 ppm (t of d); J_{AB} = J_{BD} = 10.26 Hz, J_{AD} = 0.88 Hz, J_{AC} = 0, J_{BC} = 4.40 Hz, J_{CD} = 6.10 Hz. Anal. Calcd for $C_9F_{18}O$: C, 23.19; F, 73.37. Found: C, 22.33; F, 71.16.

1-Fluoro-2-2,4,4-tetramethyl-3-pentanone. $(CH_3{}^A)_3CC(O)(CH_2{}^BF^C)(CH_3{}^D)_2$: IR (cm^{-1}) 2980 (m), 2950 (s), 2900 (m), 2870 (m), 1680 (s), 1475 (s), 1360 (s), 1290 (s), 970 (s). Major mass cations were [m/e(int.)formula]: [CI] 161(4)$C_9H_{18}OF$, M+H; 103(28)C_5H_8OF; 101(46)C_5H_6OF; 59(100)C_2FO: [EI] 69(30)C_5H_9; 57(23)C_4H_9; 44(71)C_2H_4O; 32(100)CH_2F. ^{19}F NMR (1% CFCl$_3$/CDCl$_3$/.2% CHCl$_3$) ϕ_C = -221.76 ppm (t); ^1H NMR δ_A = +1.24 ppm (s), δ_B = +4.40 ppm (d), δ_D = +1.29 ppm (s); J_{CH_2F} = 47.4 Hz.

Acknowledgement

TABLE 1

TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS[a]

Starting Compound	Fluorine Flow mL/m Reactor Mod. 1	Mod. 2	Helium Diluent mL/m Reactor Mod. 1	Mod. 2	Reaction Temp. °C Reactor Mod. 1	Mod. 2		Main Helium Carrier mL/m	Hydrocarbon Throughput millimoles/hr (H.C.carrier)	Overall[b] stoichiometry hc:F_2	Percent F_2 Conc. Final Stage	Reaction Time[c] Sec.	Product Distribution % Collected	Product Yield % Theoretical
3,3-Dimethyl-2-butanone	10	20	150	150	-40°	-30°	10°	600	2.8[e]	1:52	3.6%	49	23%	12%
2,2,4,4-Tetramethyl-3-pentanone	20	20	150	150	-30°	-20°	10°	600	2.9[e]	1:67	4.8%	49	71%	92[d]%

[a]See references 1 and 25 for the significance of these parameters.

[b]One milliliter/minute F_2 delivers 2.44 mmol/h F_2.

[c]Reactor volume/total flows; reactor volume = 1355 cc.

[d]Product is F-2,2,5-Trimethyl-3-hexanone.

[e]Total carrier flow through evaporator 550 mL/m (500 mL/m Primary, 50 mL/m secondary).

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